Green Sustainable Process for Chemical and Environmental Engineering and Science
Plant-Derived Green Solvents: Properties and Applications

2021, Pages 229-251

Chapter 14 - Plant-derived alkyl phenol as green solvents: Properties and applications

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https://doi.org/10.1016/B978-0-12-821886-0.00011-7

Abstract

The principles of green chemistry aim to minimize the consumption of energy with the application of green solvents from renewable resources, without compromising the quality of the final product. Bio-based solvents can be derived from biomass such as forest products, wood, lignocellulosic wastes, energy crops, or aquatic biomass, and are produced in biorefineries through biomass conversion methods in combination with power generation, chemicals, and fuels production. Alkylphenols are an important class of aromatic compounds produced by depolymerization of lignin (biopolymer of phenylpropanoid that gives mechanical strength to the structure of plants). Alkylphenols are generally in solid form at 258 °C, and the properties are influenced by the configuration and size of the alkyl group, the position on the ring, and the purity. The combination of hydrogenolysis and the second step of hydrodeoxygenation for lignin depolymerization has been successful to produce phenolic-based compounds. Catalytic hydrogenolysis is effective to achieve the ether bonds cleavage and enhance the hydrogen content. Catalyst-based hydrodeoxygenation could produce the products that possess low oxygen content, less amount of functional groups, and high chemical stability. Alkylphenolic solvent has great potential as an alternative t nondegradable solvent. However, excessive use of alkylphenols could lead to serious health issues and also affect the environment. Alkylphenols have been found to accumulate in aquatic organisms and more research is needed on the uptake and decomposition in humans, animals, and plants.

Previous

Next

Keywords

Green extraction; Bio-based solvent; Alkylphenols; Lignocellulosic biomass; Oil-derived synthesis; Lignin-derived synthesis; Hydrogenolysis; Hydrodeoxygenation

1. Introduction

Green chemistry necessitates the invention, planning, and implementation of chemical substances and procedure to minimize or eliminate the application and creation of harmful substances. Green extraction relies on the protocols which will minimize the consumption of energy, allow the application of substitute solvents from renewable resources, while guaranteeing a high level of final product quality [1], [2]. The six principles of Green Chemistry are: Principle 1: Innovation by selecting diversity and applying plant recyclable resources; Principle 2: Application of substitute solvents, mainly agro-solvents or water. Principle 3: Reduction of energy usage by recovery of energy and utilizing innovative high-tech; Principle 4: Formation of coproducts in place of residual waste to encompass agro and biorefineries; Principle 5: Reduction of unit operation to provide secure, strong, and managed processes; and Principle 6: Aims toward a nondenatured and recyclable (biodegradable) product having no pollutant. The principles 1, 2, 4, and 6 emphasize on meeting the agenda of Global Sustainable Development goals, while the principles 3 and 5 address the issues of economics and emission for substantial decrease of energy and time [3]. To meet the requirements of the regulations and market, the product has to achieve certain quality criteria such as being harmless to consumers and the environment, well-determined physiochemical characteristics, and ability for long-term storage [2].

Current methods of product extraction are replete with environmental concerns due to the utilization of hazardous solvent, the requirement for energy reduction, and minimizing the CO_2 release. Conventional solvents derived from fossil fuel in traditional refineries have now been met with alternatives from environmentally friendly plant-derived solvents (bio-based solvents). Bio-based solvents can be derived from biomass such as forest products, lignocellulosic waste materials, energy crops such as corn, and aquatic biomass such as microalgae. The solvents are recyclable and biodegradable, and are produced in biorefineries where biomass conversion methods are combined with power generation, chemicals production, and fuels from biomass [4], [5]. The potential applications are in p paints and coatings, household care, printing inks, adhesives, and cosmetics [6] (Fig. 1). The selection of a suitable bio-based solvent depends on parameters such as solubility or reaction rate, but the major considerations will be because of the environmental merits. The challenges will be to develop a specific solvent for specific utilization or in particular separation or extraction methods [4].

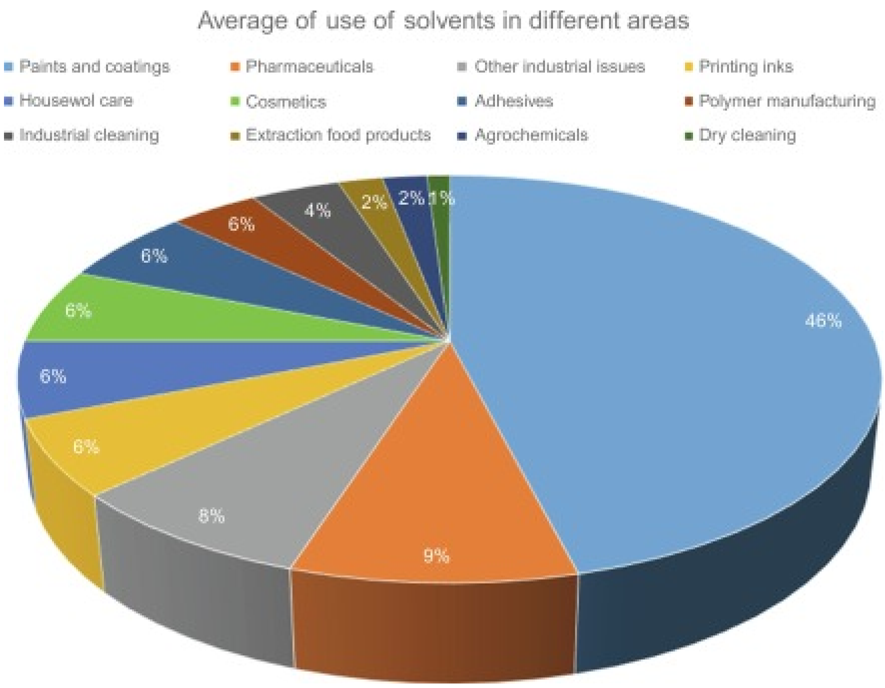

Fig. 1. Average of use of solvents in different fields.

(Modified from reference J.H. Clark, T.J. Farmer, A.J. Hunt, J. Sherwood, Opportunities for bio-based solvents created as petrochemical and fuel products transition towards renewable resources, Int. J. Mol. Sci. 16 (2015) 17101–17159.)

Alkylphenols are an important class of aromatic compounds produced by depolymerization of lignin [7]. The common structure of general alkylphenol and the structures of some alkylphenols are shown in Fig. 2, and the names according to the Chemical Abstract Service (CAS) numbers, abbreviations, types, and nature are given in Table 1. Alkylphenols are organic subtances and can be produced by, for example, corn lignin which is made to undergo solvolysis to generate 24 wt% alkylated monolignins, of which 46% is 4-ethylphenol generated from H-subunits [8]. Alkylphenol can be utilized in the making of lubricant (oil) additives, dish and laundry soaps or detergent, solubilizers, and emulsifiers [9]. The production principally involves catalyst-based alkylation of cresols, xylenols; or phenols with easily available olefins such as cyclohexanol applied as an alkylating agent; or phenols with methanol or benzyl chloride if the desired olefin is not available. Other methods for alkylphenols production are less significant than the alkylation method [10].

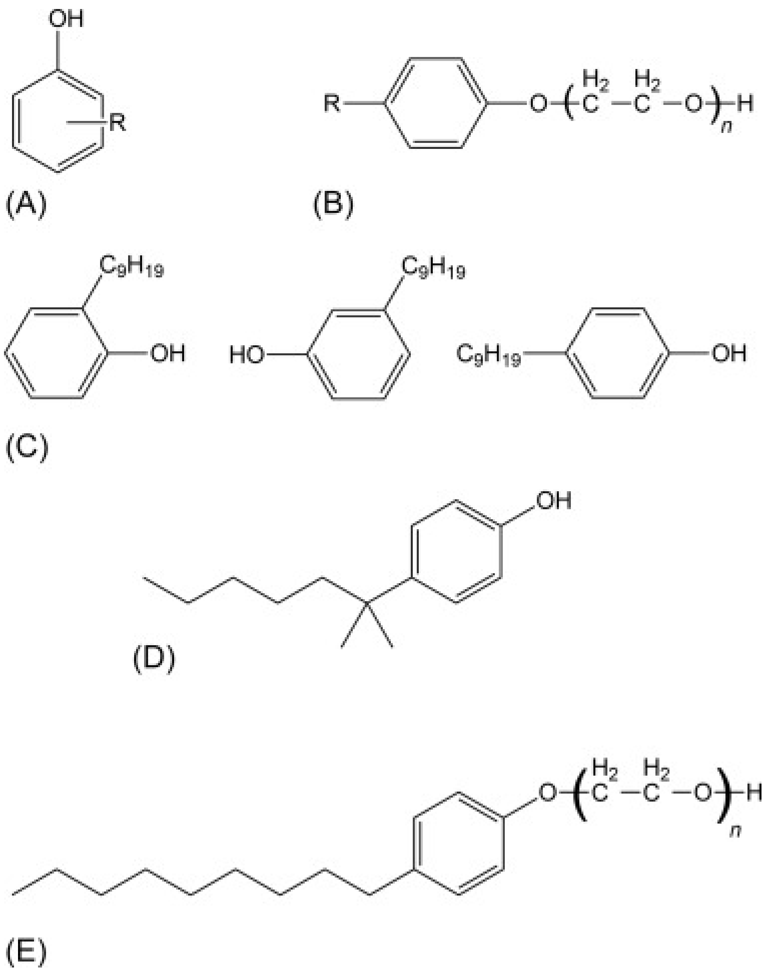

Fig. 2. General structures of (A) alkylphenol, (B) alkyl ethoxylate, (C) nonylphenol (mixture), (D) 4-*tert*-octylphenol, and (E) polyethoxylate-4-nonylphenol.

(Modified from reference A. Priac, N. Morin-Crini, C. Druart, S. Gavoille, C. Bradu, C. Lagarrigue, G. Torri, P. Winterton, G. Crini, Alkylphenol and alkylphenol polyethoxylates in water and wastewater: a review of options for their elimination, Arab. J. Chem. 10 (2017) 3749–3773.)

Table 1. Chemical Abstract Service (CAS) numbers, names, abbreviations, structure, and nature of common alkylphenols.

CAS number	**Name**	**Abbreviation**	**Structure**	**Substance**	**Formula**
25154-52-3	Nonylphenol	*n*-NP	Linear	Mixture	$C_{15}H_{24}O$
84852-15-3	4-Nonylphenol	4-NP	Linear or branched	Mixture	$C_{15}H_{24}O$

CAS number	Name	Abbreviation	Structure	Substance	Formula
104-40-5	4-*n*-Nonylphenol	4-*n*-NP	Linear	One isomer	$C_{15}H_{24}O$
26027-38-3	Polyethoxylate 4-nonylphenol	4-NPnEOs	Linear	Mixture	$(C_2H_4O)_nC_{15}H_{24}O$
28679-36-3	Nonylphenol monethoxylate	NP1EO	Linear	Mixture	$C_{17}H_{28}O_2$
27176-93-8	Nonylphenol diethoxylate	NP2EO	Linear	Mixture	$C_{19}H_{32}O_3$
104-35-8	4-Nonylphenol monethoxylate	*n*-4-NP1EO	Linear	–	$C_{17}H_{28}O_2$
20427-84-3	4-*n*-Nonylphenol diethoxylate	*n*-4-NP2EO	Linear	–	$C_{19}H_{32}O_3$
140-66-9	4-Octylphenol	*t*-4-OP	Branched	One isomer	$C_{14}H_{22}O$
1806-26-4	4-*n*-Octylphenol	*n*-4-OP	Linear	One isomer	$C_{14}H_{22}O$
2315-67-5	Octylphenol monethoxylate	*t*-4-OP1EO	Branched	–	$C_{16}H_{26}O_2$
2315-61-9	Octylphenol diethoxylate	*t*-4-OP2EO	Branched	–	$C_{18}H_{30}O_2$

Data from reference Z. Mahmood, M. Yameen, M. Jahangeer, M. Riaz, A. Ghaffar, I. Javid, Lignin as natural antioxidant capacity, in: M. Poletto (Eds.), Lignin—Trends and Applications, Elesevier, 2018, pp. 181–205.

2. Properties, stability, and toxicity of alkylphenols

2.1. Physical properties

The physical characteristics of alkylphenols are comparable to those of phenols. The properties can be affected by the type of alkyl substituent and the location of substituent on the ring. Like phenols, alkylphenols are generally in solid form at 258°C, and the physical form is influenced by the configuration and size of the alkyl group, the position on the ring, and the purity. In their pure form, these are colorless, pale yellow, or white. The physical properties are listed in Table 2. The para substituted alkyl phenols possess greater boiling and melting points as compared to the ortho-alkylphenols where the para-alkylphenols reach a maximum melting point limit and then reduce for the ter-butyl structure. For a low melting point, the alkylphenols are produced from an alkene brook comprising a mixture of isomers. Alkylphenols possess a waxy texture in which the carbon chain of alkyl groups units. With di- and tri- substituents attached, the alkylphenols are apt to supercool. Like phenols, alkylphenols have high sensitivity toward oxidation, where a minute quantity of alkaline or metal impurities could alter the oxidation, resulting in discoloration caused by the oxidation products.

Table 2. Physical properties of common alkylphenols.

Name	Molecular formula	Molecular weight	Physical form at 25°C	Boiling point (°C)	Freezing point (°C)	Density (g/mL)	Flash point (°C)
4-*tert*-Amylphenol	$C_{11}H_{16}O$	164	Solid	249	90	0.915	121
4-*tert*-Butylphenol	$C_{10}H_{14}O$	150.2	Solid	237	97	0.890	117
2-Sec-butylphenol	$C_{10}H_{14}O$	150.2	Liquid	224	20	0.938	> 93
4-Cumylphenol	$C_{15}H_{16}O$	212	Solid	335	70	1.029	188
4-Dodecylphenol	$C_{18}H_{30}O$	262	Liquid	334	–	0.914	> 100
4-Nonylphenol	$C_{15}H_{24}O$	220.3	Liquid	310	–	0.933	146
4-*tert*-Octylphenol	$C_{14}H_{22}O$	220.3	Solid	290	81	0.940	132
2,4-Di-*tert*-amylphenol	$C_{16}H_{26}O$	234.4	Liquid	275	23	0.900	104
2,4-Di-*tert*-butylphenol	$C_{14}H_{22}O$	206.3	Solid	263	52	0.867	115
2,6-Di-*tert*-butylphenol	$C_{14}H_{22}O$	206.3	Solid	253	36	0.898	> 99
Di-sec-butylphenol	$C_{14}H_{22}O$	206.3	Liquid	–	–	0.902	127
2,4-Dicumylphenol	$C_{24}H_{26}O$	330	Solid	–	65	1.030	462
2-Methylphenol	C_7H_8O	108.1	Solid	191	30	1.049	81
3-Methylphenol	C_7H_8O	108.1	Liquid	202	10	1.042	86
4-Methylphenol	C_7H_8O	108.1	Solid	202	34	1.022	86

Name	Molecular formula	Molecular weight	Physical form at 25°C	Boiling point (°C)	Freezing point (°C)	Density (g/mL)	Flash point (°C)
2,6-Dimethylphenol	$C_8H_{10}O$	122.1	Solid	203	48	1.020	88

Data from reference H. Fiege, H.W. Voges, T. Hamamoto, S. Umemura, T. Iwata, H. Miki, Y. Fujita, H.J. Buysch, D.G.W. Paulus, Phenol derivatives, in: W. Gehartz, G.S.T. Kellersohn, B. Elvers, S. Hawkins, U. Winter (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2000, pp. 521–582.

Alkylphenols are soluble in basic organic solvents such as alcohols, acetone, toluene, and hydrocarbons where the solubility in organic solvents such as heptane or alcohol is due to “like dissolves like.” The higher the polarity of alkylphenols, the higher their solubility in alcohols, but not in aliphatic hydrocarbons, and similar is the case with xylenols and cresols. Pure phenols that are para substituted, C3 through C8, can be produced from heptane via crystallization [11]. Alkylphenols possess acidic characteristics to the hydroxyl group due to the presence of an aromatic ring having pK_a of raw alkylphenols at 10–11 [12]. Unsubstituted alkylphenols in ortho location solubilize in caustic aqueous solution. When the carbon atoms attached to the ring grow, the solubility in water drops. The solubility of alkaline phenolatic salt in water also reduces with the increment in the number of carbon atoms in the alkyl chain of alkylphenols. However, the increment in the carbon atom number of the carbon (alkyl) chain in alkylphenols will increase their solubility in hydrocarbons. The extractions (aqueous caustic) of alkylphenols from an organic medium can be attained at higher temperatures. Huge substituents at the ortho position minimize the alkali phenolate solubility in water, a phenomenon known as cryptophenol. Potassium hydroxide solution (35%) in methanol, which is known as Claisen's alkali, solubilizes these hindered phenols [13].

2.2. Stability and toxicity

Phenol compounds like nonylphenol (NP), octylphenol (OP), and bisphenol A (BPA) are xenobiotics, toxic and harmful, but quite stable in the environment. The existence of alkylphenols in the environment is attributable to the alkylphenol ethoxylates (APEs) degradation [14]. These alkylphenols are the basic extracts in the chemical industry, applicable as surfactants in the production of nonionic detergents, or in disinfectants and cosmetic industries [15]. Annual production of alkylphenols in the United States has been reported at 154,000 tons [16]. The most important types are octylphenol ethoxylate and nonylphenol ethoxylate. The degradation mechanism in the environment and the loose side chains of ethylene oxide later turn into alkylphenols (4-*n*-nonylphenol and 4-*n*-octylphenol). Unlike many exogenous substances, alkylphenols enhance their toxicity during the biodegradation process [15]. Phenolic derivatives such as short chain alkylphenols, comprising a minimum one alkyl group, having a chain length from C1 to C3, are strongly soluble in water. These do not adsorb easily on the solid particles, thereby increasing the risk of pure drinking water pollution [17].

Alkylphenols are known as endocrine disrupting compounds and may result in the development and reproduction disorder in living organisms. A study on the endocrine disrupting nature of alkylphenols has been conducted on *Daphnia magna* where exposure to various amounts of 4-nonylphenol and bisphenol A has resulted in severe developmental effects on the aquatic organism [18]. Octylphenol has great solubility in lipids and can flow into the human's internal organs through cell membranes to cause severe harmful health effects, including endocrine system disruption [19]. The existence of bisphenol A and other alkylphenols in the environment is due to the anthropogenic activities like landfilling, recycling of sewage sludge, and treatment of wastewaters [20], [21]. Some phenolic derivatives are found in sewage sludge, released components from sewage treatment plants, groundwater and soil, and sediments and river water [22]. While the concentration of these phenolic derivative compounds in the environment is depleting, they are still discovered in microgram per liter concentration in water bodies and in milligram to per kilogram in soil and sediments [9], [23], [24]. The presence of bisphenol A, octylephenol, and nonylphenol at higher amounts and their toxicity requires strict monitoring and evaluation on all spheres [25].

3. Production and processing

3.1. Oil-derived synthesis

Biomass is a low-cost, low pollution, and renewable bioresource with a high content of carbon, negligible amount of nitrogen and sulfur, and is therefore capable of substituting petroleum-derived fuels [26], [27]. However, the huge limitation of biomass is its low density of energy, and the process such as fast pyrolysis could generate greater high-valued heating liquid to be extracted continuously, known as bio-oil [28]. More than 300 compounds have been utilized to produce bio-oil and they include lignin-derived oligomers, phenols, furans, alcohols, aldehydes, and carboxylic acids [29]. Poor chemical stability and substantial oxygen content differentiate bio-oil from petroleum fuels, making more refining a requirement to make bio-oil a suitable alternative [30]. Hydrodeoxygenation is an important step toward upgrading the low-level products to bio-oil [31], [32], based on the deoxygenation of biofuel substances with the use of a catalyst and introduction of hydrogen [33]. The approach of upgrading the biofuel via hydrodeoxygenation stabilizes the final product and eliminates oxygen [34]. A strongly active catalyst with 2% (w/w) Ru/TiO_2 dispersion, prepared following a photochemical process at room temperature, has served effectively in the hydrodeoxygenation of phenol-based compounds and biofuel production due to greater Ru dispersion. Different phenol-based compounds such as phenolic dimers and monomers could be converted into respective hydrocarbons with a maximum yield of almost 100%. The catalyst is also effective in upgrading the biofuel made from cotton straw pyrolysis which is rich in phenol-based compounds. A total of 57.6% of alkylphenols and 32.4% of hydrocarbons is obtained at 280°C from the bio-oil, and the composition of alkylphenols and hydrocarbons has great potential for usage as chemicals and fuels [31].

3.2. Alkylphenols from lignin

FEEDBACK

Cell walls of plants are made up of lignin which is a biopolymer made up of phenylpropanoid that gives mechanical strength to the structure of plants. Lignin is the major component of terrestrial plant cell walls. The lignin structure (Fig. 3) strengthens the plant cell wall, promotes transport of water, and functions as a physical barrier against different pathogens. Lignin comprises syringly (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units which are derived from the polymerization of sinapyl alcohol, confieryl alcohol, *p*-coumaryl alcohol, and hydroxycinnamyl alcohol. Lignin is also derived from many monomers of aromatic compounds [35], and is used in the production of binding agents, sequestrant agents, emulsifying or dispersing agents, and as a raw material for different types of synthetic polymers like formaldehyde-phenol resin, polyurethane resin, polyester, and epoxy resin. Lignin is a potential source of different chemicals and aromatic products, while chemically modified lignin can be utilized as a reinforcing material or filler in the polymer blends and composite materials [36].

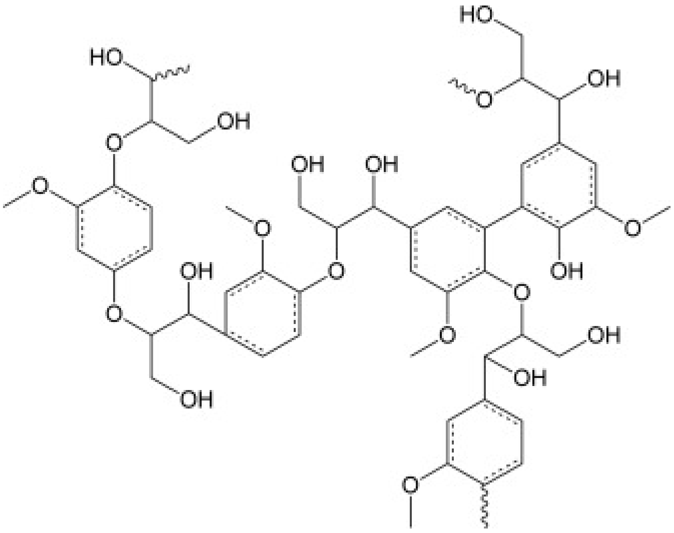

Fig. 3. Structure of lignin.

(Modified from reference Z. Mahmood, M. Yameen, M. Jahangeer, M. Riaz, A. Ghaffar, I. Javid, Lignin as natural antioxidant capacity, in: M. Poletto (Eds.), Lignin—Trends and Applications, Elesevier, 2018, pp. 181–205.)

Depolymerization of lignin to phenolic compounds or monomers (Fig. 4) can be achieved by a different liquid acid and base catalyst. Homogenous catalysts include sulfuric acid, phosphoric acid, and hydrochloric acid, while heterogeneous catalysts include carbonaceous solid acids prepared via the hydrothermal operation of cellulose, lignin, and glucose. A solvent mixture of ethanol/1,4-dioxane/formic acid (FA) has been tested where ethanol acts as a solvent or reactant for an in situ hydrogen donor, 1,4-dioxane as a lignin solvent, and formic acid as an in situ hydrogen donor and catalyst. At a composition of ethanol/1,4-dioane/formic acid at the ratio of 10:10:2 (v/v), the lignin conversion has resulted in a 22.4% yield of phenolic monomers and 6.57% residual yield at 300°C [37]. However, these homogenous and base catalysts may corrode the equipment in which highly efficient catalysts are required. Solid acid catalysts are eco-friendly, noncorrosive in nature, relatively safer, much more convenient to be isolated and recovered as compared to the homogenous catalysts, and highly effective to depolymerize lignin into much higher valued products/extracts [38], [39]. The depolymerization of lignin separated via the organosolv fractionation of bagasse with the aid of different homogenous and heterogeneous catalysts has shown maximum phenolic monomers attained from carbonaceous solid acids which are active and efficient catalysts with the highest stability even after five continuous cycles [40]. The product separation after the depolymerization reaction is shown in Fig. 5.

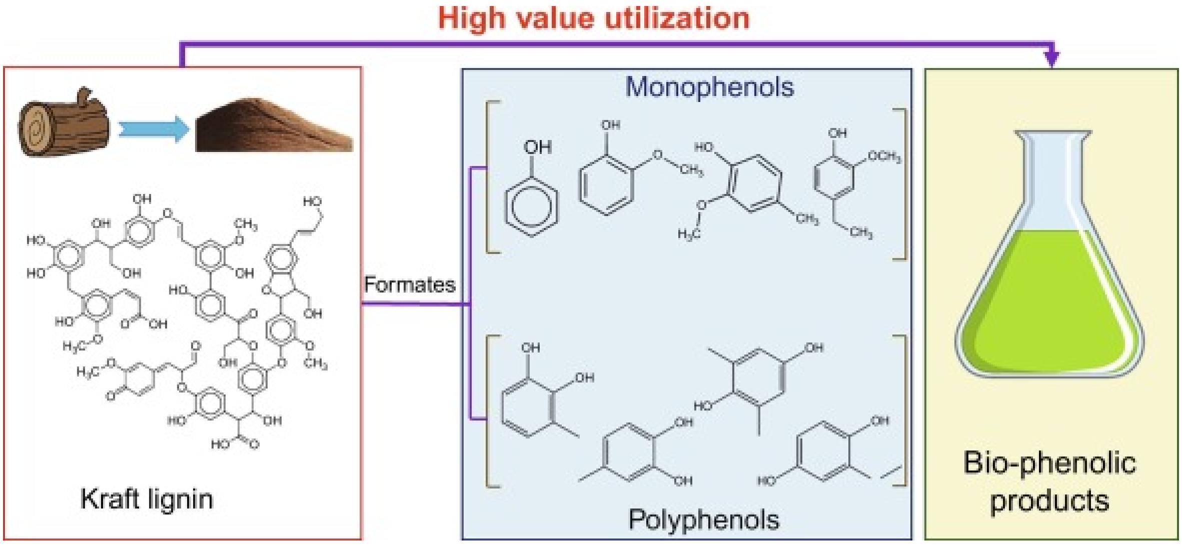

Fig. 4. Conversion of Kraft lignin into bio-phenolic products.

(Modified from reference W. Wang, M. Wang, J. Huang, X. Zhao, Y. Su, Y. Wang, X. Li, Formate-assisted analytical pyrolysis of kraft lignin to phenols, Bioresour. Technol. 278 (2019) 464–467.)

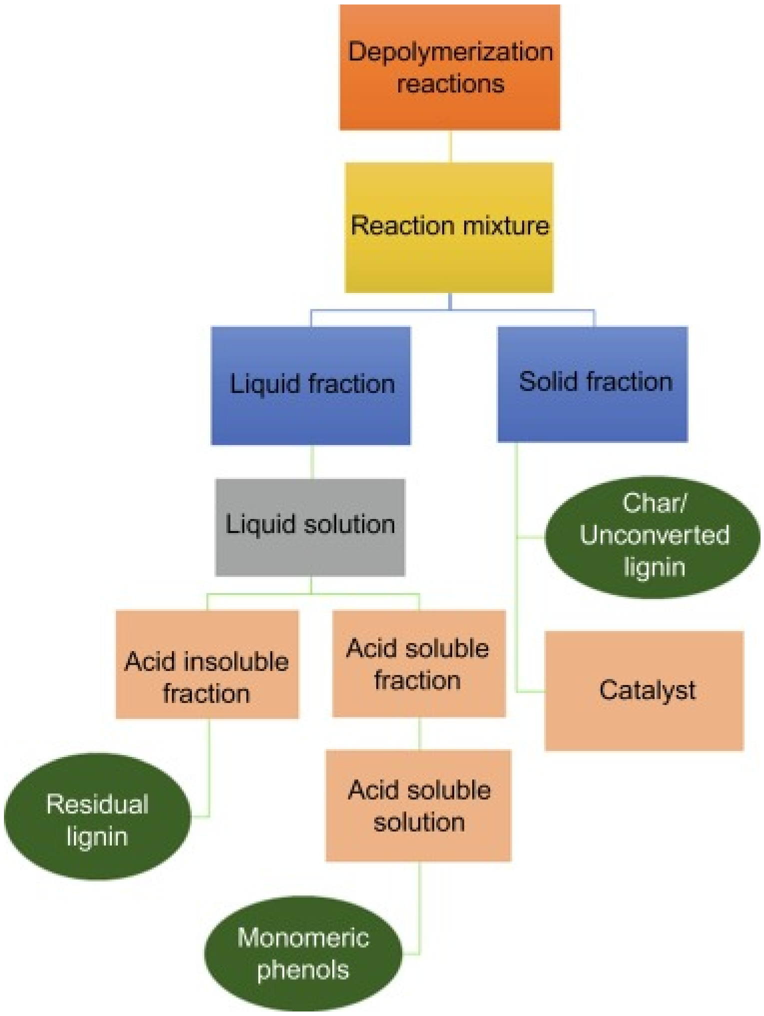

Fig. 5. Illustration of products derived from depolymerization of a lignin biomass.

(Modified from reference P. Asawaworarit, P. Daorattanachai, W. Laosiripojana, C. Sakdaronnarong, A. Shotipruk, N. Laosiripojana, Catalytic depolymerization of organosolv lignin from bagasse by carbonaceous solid acids derived from hydrothermal of lignocellulosic compounds, Chem. Eng. J. 356 (2019) 461–471.)

Zeolites have been widely applied as solid acid catalysts because of their significant topological morphology, changeable pore structures, large surface area, and adjustable acidity of BrØnsted and Lewis acid sites. Zeolites possess great hydrothermal stability, limiting effects in pores, electric field properties, and high adsorption capacity which are all attractive features for applications in laboratories and industries. These are advantageous as the metallic support system to upgrade lignin from lignin derivatives [39]. The valorization of lignin has been achieved via fast pyrolysis with the utilization of ZSM-5 zeolites with variable acidic properties and porosity. The mesoporous ZSM-5 (9 nm), nano-sized ZSM-5 (< 20 nm), and conventional microporous ZSM-5 are evaluated as catalysts in a fixed-bed reactor at 400–600°C to depolymerize lignin into high-valued phenolic components. The conventional ZSM-5 zeolites show higher selectivity toward mono-aromatics, while the nano-sized and mesoporous ZSM-5 zeolites show high selectivity for alkylphenols [41]. A $WO_3/\gamma Al_2O_3$ catalyst mad incipient wet impregnation process achieves considerable conversion of enzymatically hydrolyzed lignin into different alkylphenols (Fig. 6) in the presence of supercritical ethanol. Lignin is fully dissolved and transformed into aromatic and aliphatic products at 320°C with 363.4 mg/g total yield where the aromatic products are 315.8 mg/g lignin, representing 86.9% of the total products yield, and 67.5% selectivity of alkylphenols [42].

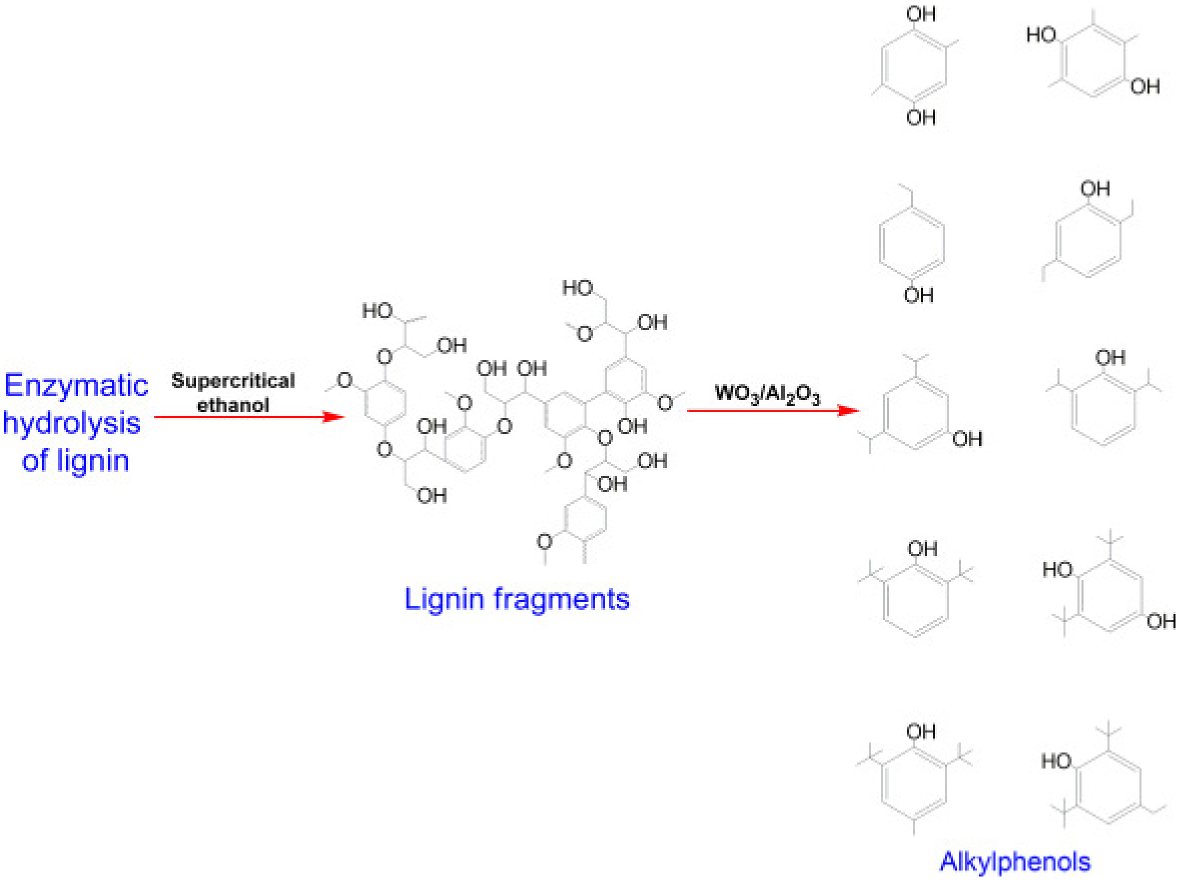

Fig. 6. Conversion of enzymatic hydrolysis lignin into different alkylphenols using a catalyst.

(Modified from reference F. Mai, Z. Wen, Y. Bai, Z. Ma, K. Cui, K. Wu, F. Yan, H. Chen, Y. Li, Selective conversion of enzymatic hydrolysis lignin into alkylphenols in supercritical ethanol over a $WO_3/\gamma\text{-}Al_2O_3$ catalyst, Ind. Eng. Chem. Res. 58 (2019) 10255–10263.)

3.3. Bio-based phenols from lignocelluloses

Lignocellulosic biomass is an abundant recyclable carbon resource from which lignin as a significant component can be derived. Chemically, the lignocellulosic biomass comprises 5%–25% lignin, 10%–40% hemicellulose, and 40%–80% cellulose. Hemicellulose and cellulose comprise polymers based on sugar monomers that are galactose, glucose, xylose, mannose, rhamnose, and arabinose, whereas lignin is made up of different units of methoxylated phenylpropanoid, which therefore could provide alternative resources of aromatic compounds [43]. The fibrous nature of lignocelluloses from biorefineries as agricultural by-products, grasses, municipal solid waste, and wood residue ensures sustainable supply for long-term utilization [43], [44]. The alkylmethoxyphenols that are derived from the pheny which are connected in a random manner via C—O—C and C—C bonds in lignin, are generally functionalized phenols at the para position with an alkyl group such as propyl and methoxy groups at both or one of the ring ortho positions. Their excessive functionalization characteristics have limited their applications in different fields. These alkylmethoxyphenols could be selectively transformed into phenols involving demethoxylation and dealkylation. The demethoxylation route is difficult to prevent aromatic ring hydrogenation and elimination of the hydroxyl group of the phenolic parts. Dealkylation usually forms olefins on the acid catalysts that are resistant to oligomerization. Another approach involves the conversion of alkylmethoxyphenols to phenols aimed at combining demethoxylation with transalkylation of the alkyl groups into a benzene feedstock that produces propylbenzene, cumene, and toluene as coproducts (Fig. 7). Cumene and toluene can be upgraded to highly efficient xylenes using advanced technologies.

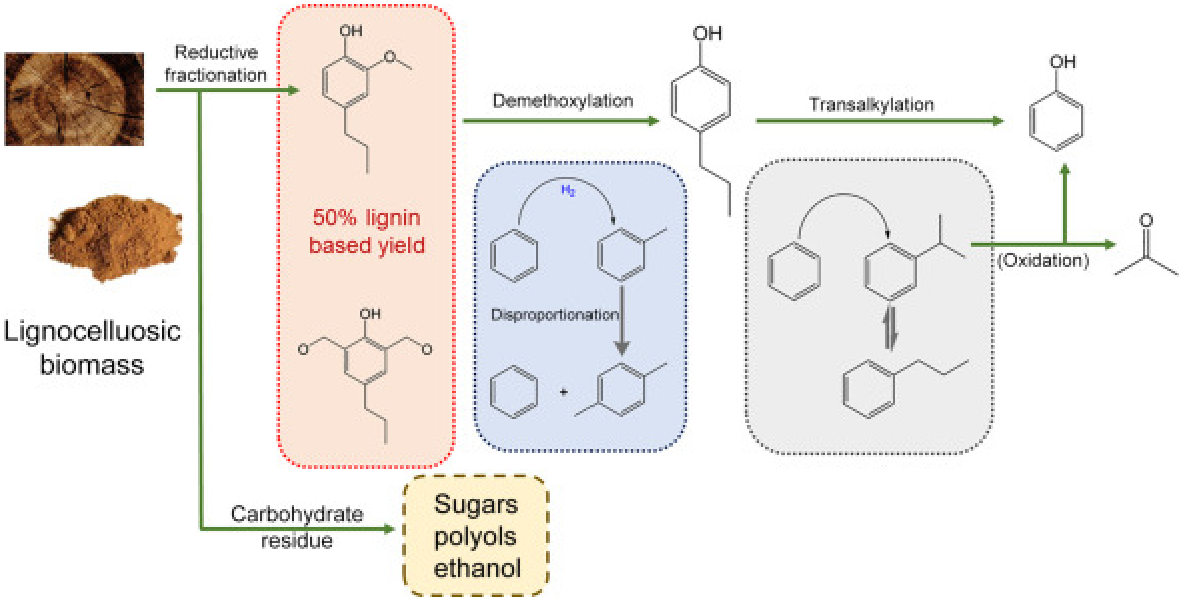

Fig. 7. Routes for the production of phenols from the lignin part of a lignocellulosic biomass.

(Modified from reference X. Huang, J.M. Ludenhoff, M. Dirks, X. Ouyang, M.D. Boot, E.J.M. Hensen, Selective production of biobased phenol from lignocellulose-derived alkylmethoxyphenols, ACS Catal. 8 (2018) 11184–11190.)

Lignin-derived phenols are usually substituted by mixtures of different functional groups that require more catalytic reactions to generate phenol. A close contact between a demethoxylating catalyst based on gold nanoparticles, assisted by titanium oxide, and a transalkylating catalyst based on HZSM-5 has produced 60% phenolic yield from 4-propylgluaiacol in one step [45]. A batch type reactor has been used to investigate the transalkylation of para-propylphenol, a lignin-derived compound, with MFI-type zeolite catalysts and benzene solvent. The three-dimensional nonfunctionalized catalyst exhibits high activity for para-propylphenol transalkylation producing phenol along with C3-benzene which includes cumene and propylbenzene as major products. The time for r than 2 h at 400°C with continuous reactions after C3-benzene and phenol formation, resulting in lower product selectivity, and no heavy components formed from the polymerization processes. Benzene plays an important role in suppressing the coke formation on the zeolite catalyst under critical conditions. The method can therefore be used for the co-production of alkylated benzene and phenols from lignin-derived phenols [46].

Transalkylation is an innovative technique to produce phenol from alkylphenols. Alkylated benzene is coproduced when benzene is applied as an alkyl group recipient, which can further be used as gasoline additives or fuels for jet because of the high octane number and high calorific value [46]. The major challenge is to process the alkylated phenols which will account as a major process in the coal-fuel and wood biorefineries. An effective zeolite-based method could transform mixtures of ethyl and propylphenols into high-valued phenols and related olefins, propylene, and ethylene, with the potential to attain a tenfold higher phenol yield relative to the one-step method consolidated with lignin depolymerization. However, the issue with zeolites (H-USY) having large pore sizes is that they are not selective and deactivate quickly. A medium pore size H-ZSM-5 zeolite enables higher selectivity with a longer catalyst life, and water as a medium plays a crucial role. Dealkylation with high efficiency and robustness has been achieved utilizing bare metal free zeolite ZSM-5 catalysts along with the water medium. The catalysis studies explore the origin of the selection of shape in nature and the competitive adsorption of phenols and water and provide understanding on the functionality existing within the biomass [47].

3.4. Bio-based chemicals from integrated biorefineries

Lignocellulosic biomass-based feedstocks, which include the agro waste wood chips, are a low-cost and recyclable resource for large-scale commercial biorefineries due to their abundance and availability, apart from their role in carbon sequestration [48]. The possible pathway for biorefinery chemo-catalysis is shown in Fig. 8. The generation of fuels and potential chemicals from a lignocellulosic biomass is illustrated in Fig. 9. Structurally, cellulose is composed of anhydrous units of glucose, whereas hemicellulose is composed of various sugar (C5) units. Lignin has a complex structure in three dimensions and is basically a connective biopolymer which has phenylpropanoid monomers with aromatic and hydrophobic properties. With structural and chemical composition differences, cellulose, hemicellulose, and lignin have different chemical reactivities. In these complexities, coupled with their inert chemical form and the compositional ratio of oxygen, hydrogen, and carbon in the biomolecules, there are inherent difficulties for chemo-catalytic transformation from the bio-based feedstock into different chemicals and fuels. The development of highly energetic and active catalysts for the chemo-catalytic conversion of lignocellulosic biomass into desirable products is still challenging [48]. The targeted compounds include organic acid like levulinic acid and formic acid [49], alcohols [50], and furans like furfurals and 5-hydroxymethylfurfural (5-HMF) [51]. These products can be transformed into a variety of derivatives that serve as highly potential agents in polymers, solvents, and biofuel industries.

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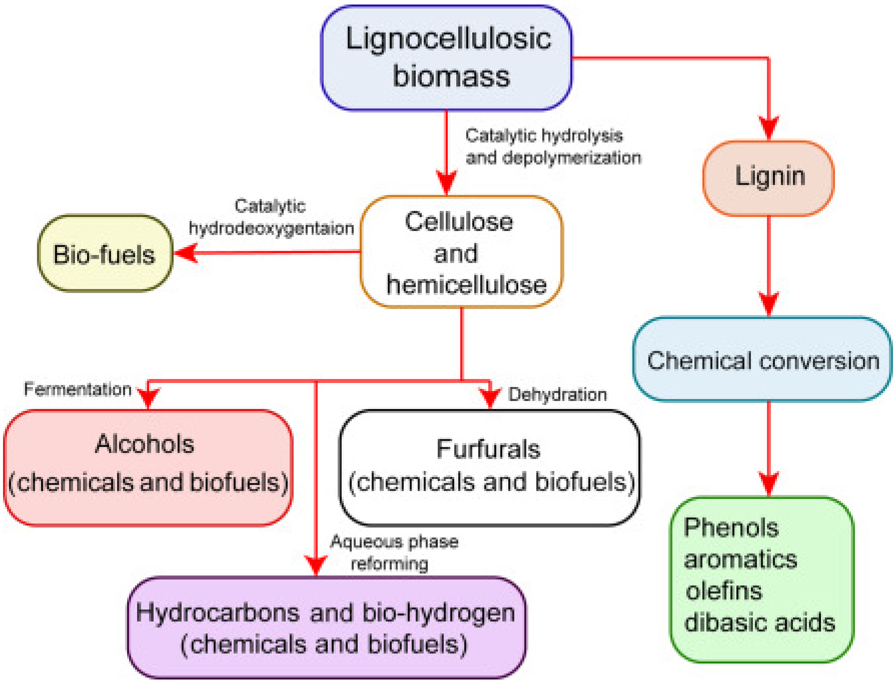

Fig. 8. A general schematic representation of a chemo-catalytic biorefinery.

(Modified from reference K. Kohli, R. Prajapati, B.K. Sharma, Bio-based chemicals from renewable biomass for integrated biorefineries, J. Energies 12 (2019) 233.)

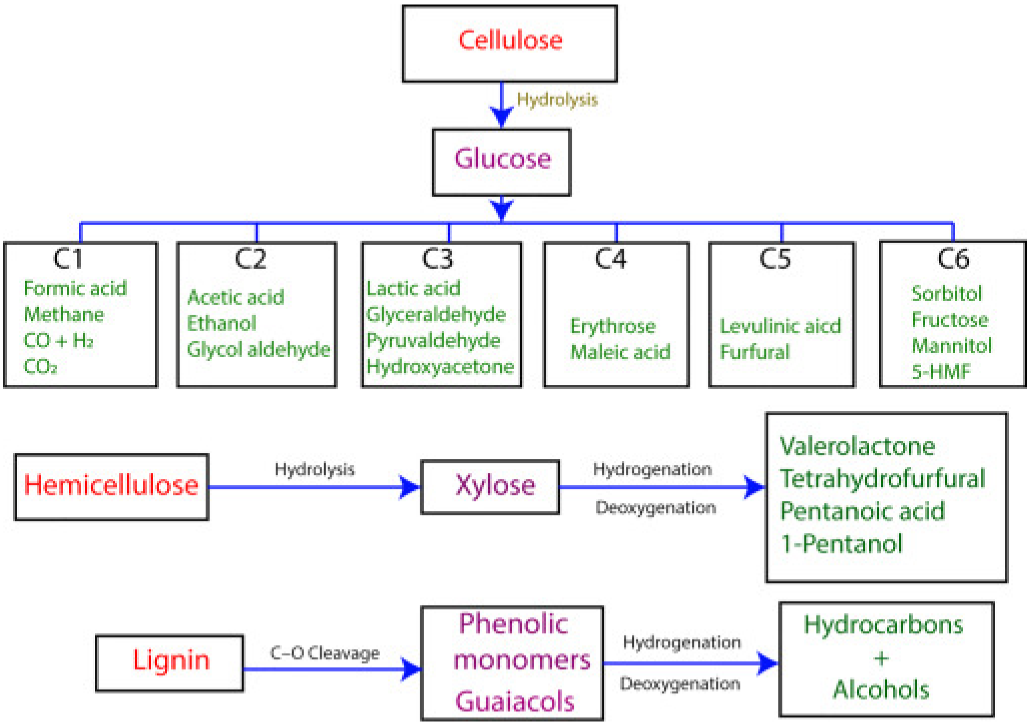

Fig. 9. Potential fuels and chemicals derived from a lignocellulose-based biomass.

(Modified from reference K. Kohli, R. Prajapati, B.K. Sharma, Bio-based chemicals from renewable biomass for integrated biorefineries, J. Energies 12 (2019) 233.)

3.5. Reactions involved in biomass conversion

3.5.1. Dehydration

Dehydration is a process that involves the removal of the water molecule from the reactant, especially alcohol, to form an alkene or other unsaturated products [52]. Dehydration is usually catalyzed with the aid of Lewis or Brønsted acids because of the strongly bonded hydroxyl group. The dehydration process involves three steps (Fig. 10): Step 1—the hydroxyl group is protonated in the presence of the Brønsted acid catalyst which is a more preferable leaving group as compared to the simple hydroxyl group. The catalyst is removed as water in the end; Step 2—according to Zaitsev's rule (the main product is always alkene with majority substitution on double bond), a double between carbon atoms is made in the carbon backbone of the substrate, while in case of the reactions catalyzed by Lewis acids, the reaction undergoes bond formation between the electrons of the lone pair of the hydroxyl group and the Lewis acid (in Step 1) [53]. The electrophilic nature of the Lewis acid reduces the density of electrons in the C—O bond of alcohol, resulting in the breaking of the C—O bond and the generation of alkene along with the Lewis acid hydroxide species (Step 2); Step 3—the hydroxide of Lewis acid combines with the released proton to form water along with the neat catalyst species [48].

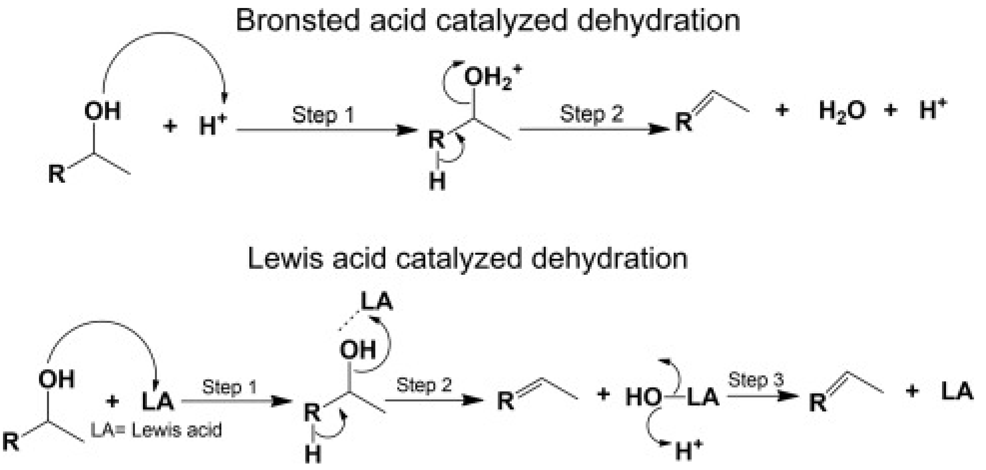

Fig. 10. Mechanism of dehydration using Lewis and Brønsted acid catalysts.

(Modified from reference K. Kohli, R. Prajapati, B.K. Sharma, Bio-based chemicals from renewable biomass for integrated biorefineries, J. Energies 12 (2019) 233.)

3.5.2. Hydrogenation

The products obtained from the dehydration process can be enhanced via hydrogenation. Hydrogenation (Fig. 11) is the principal reaction in chemistry where hydrogen atoms are added to unsaturated compounds to lower the number of triple and double bo hydrogen (H_2) in gaseous form and some other compounds that could transfer hydrogen can be utilized as a source of hydrogen in reaction. Nevertheless, hydrogen addition does not proceed in the absence of a catalyst. Heterogeneous and homogenous catalysts are used to catalyze the reaction in the shortest possible time interval. For the catalytic biomass conversion process, heterogeneous systems having solid state metal hydrogenation catalysts and molecular hydrogen are utilized [48]. Nature generates a number of unsaturated compounds containing double bonds, C═C, in carbonyl groups, and in the structures of ketoses and aldoses of hemicellulose and cellulose. Hydrogenation of the lignocellulose-biomass-based monosaccharides produces sugar alcohols [48], and hydrogenation of xylose and glucose generates xylitol and sorbitol, respectively. The products of hydrogenation can be utilized as monomers, biofuels, and solvents [54], [55], [56].

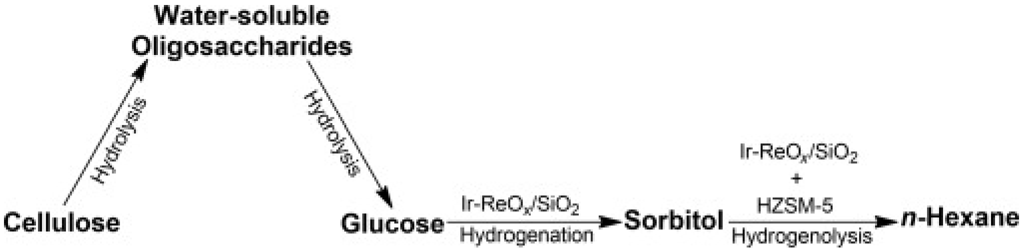

Fig. 11. Illustration of hydrogenation process.

(Modified from reference X. Han, Y. Guo, X. Liu, Q. Xia, Y. Wang, Catalytic conversion of lignocellulosic biomass into hydrocarbons: a mini review, Catal. Today 319 (2019) 2–13.)

3.5.3. Hydrodeoxygenation

Hydrodeoxygenation is a reaction which involves the elimination of oxygen from the substrate in the existence of hydrogen. The elimination of oxygen to restrain compound functionalities can take place via direct hydrogenolysis (H_2 breaks the C—O bond), dehydration (the C—O bond breaks with the elimination of the water molecule), decarboxylation (CO_2 release), and decarbonylation (release of CO) [57]. In the case of biomass-derived substrates, hydrodeoxygenation reactions are mostly used to minimize the high content of oxygen [58]. Generally, these hydrodeoxygenation reactions need high pressure and high temperature, thereby forming the product mixtures via C—C bonds breaking and rearrangements occurring in the carbon backbone (Fig. 12) [48]. Hydrodeoxygenation requires a specific catalyst to generate the desired products and the mechanisms are dependent on the type of catalysts used and the reaction conditions [48]. Noble metal containing catalysts are generally used along with the Lewis or Brønsted acidic sites for C—O bond breakage.

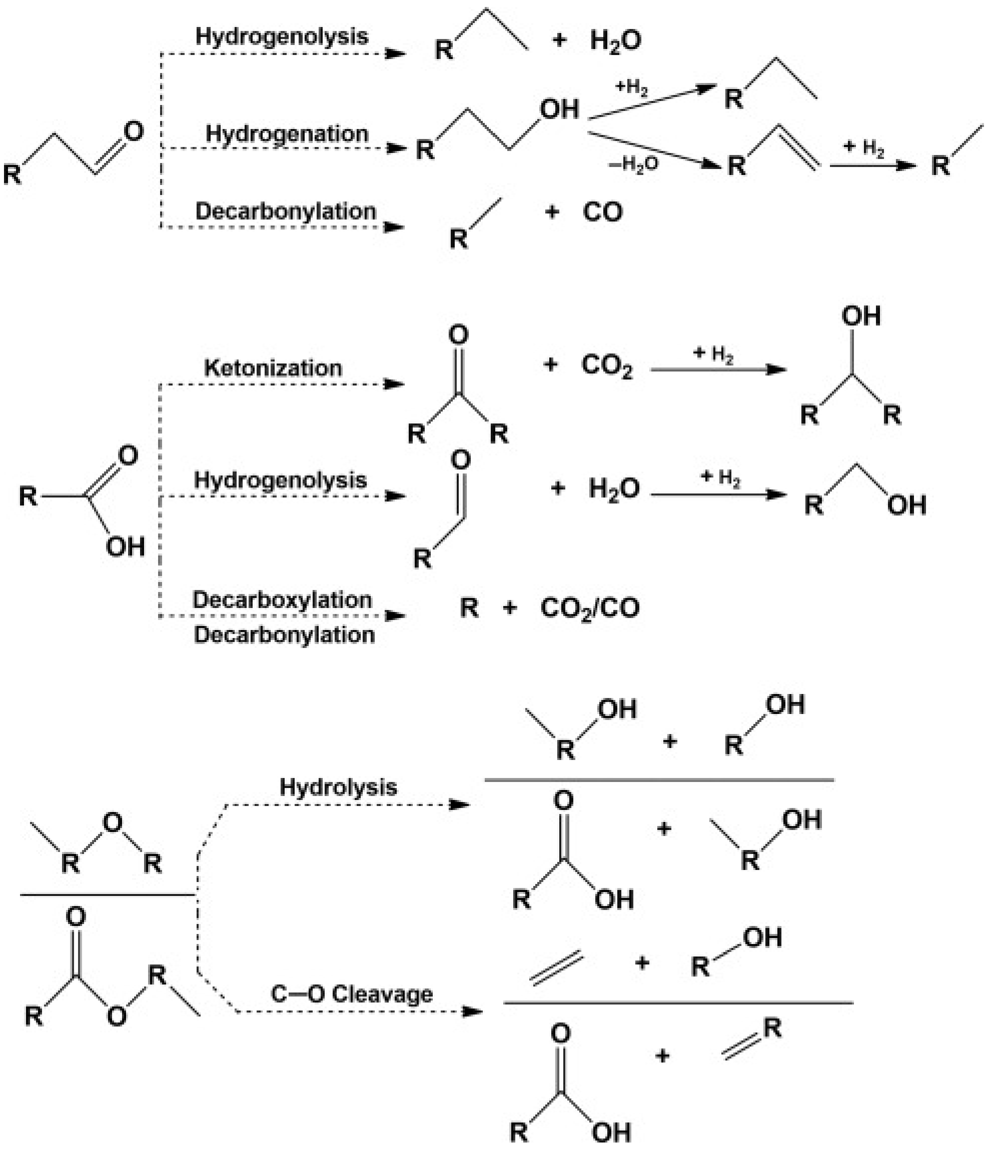

Fig. 12. Hydrodeoxygenation routes dependent on oxygen moieties.

(Modified from Z. He, X. Wang, Hydrodeoxygenation of model compounds and catalytic systems for pyrolysis bio-oils upgrading, Catal. Sustain. Energy 1 (2013) 28–52.)

3.5.4. Hydrogenolysis and hydrodeoxygenation of lignin in a two-step process

A catalytic hydrogenolysis mechanism for depolymerization of lignin is required for ether bonds cleavage and enhanced hydrogen content [40], [59], [60]. Noble metal is the most common catalyst used [61], [62], while others such as Pd/C, Pt/C, Ru/C, and Co/C@N have proven effective for the hydrogenolysis process of lignin [63], [64], [65]. Incorporation of acids in noble metals serving as bifunctional catalysts is effective in the termination of condensation and to produce stable products [66], [67]. Catalysis with phosphoric acid and Pt/C, and sulfuric acid with Pt/Al_2O_3, produces 46.4% of phenol-based monomers and 17% of guaiacol-type products, respectively, after the depolymerization of lignin [68], [69]. Similarly, catalytic combined effects of noble metals with metal chlorides have also been proven successful [62], [70], [71], [72]. The major products from the hydrogenolysis of l possess large oxygen content and a large quantity of different functional groups, and these cannot directly be utilized as fuels.

Catalyst-based hydrodeoxygenation is a successful downstream reaction to produce products that possess low oxygen content, less amount of functional groups, and high chemical stability [73], [74], [75]. Solid form catalysts for hydrodeoxygenation, comprising the metal and support system, have been mostly utilized, as these have good recyclability and product separation. Solid single-site catalysts are required to enhance the efficiency of lignin depolymerization and for C—O cleavage mechanisms [39], [76], [77], [78]. Noble metal catalysts have much more activity for hydrodeoxygenation reaction as compared to the transition metal and the sulfide metal. Unfortunately, the high cost of the catalyst restricts its vast application in different fields. Lowering the noble metal load and improving the metal sites, by enhancing the specific activity through the reduction of the metal particle size and improving metal dispersion, can help to overcome the limitation [79], [80] and elevate the efficiency of hydrodeoxygenation for phenolic compounds [81].

The combination of hydrogenolysis with the second step of hydrodeoxygenation for lignin depolymerization is an optimal solution. The first step involves lignin depolymerization via hydrogenolysis in the presence of Pd/C, and is integrated with $CrCl_3$ (metal chloride) at 280°C. The types of catalyst, time, and reaction temperature are all important factors influencing the liquefaction of lignin and the distribution of products. $CrCl_3$ is effective to catalyze the breakage of bonds and Pd/C influences the hydrogenation process. During hydrogenolysis, methylation (methanol used as the solvent), condensation, and depolymerization occur simultaneously where the condensation process is favored at high temperature and a longer time interval. In the second step, the extraction of aromatic monomers takes place in the presence of octane solvent (89.7% degree of extraction) and the high yield aromatic monomers at 19.2% are used as substrates for hydrodeoxygenation reaction [82]. The high dispersion of the 2 wt% Ru/TiO_2 catalyst in the presence of octane under 1 MPa hydrogen pressure at 300°C has been successfully utilized for lignin depolymerization to extract fuels. The products obtained after hydrodeoxygenation include a 49.7% yield of alkylphenols and a 26.5% yield of hydrocarbons consisting of 24.5% of arenes and 2% of cyclohexane. The two-step method represents a reference point for the production of fuel from lignin [81].

4. Production of biofuels using alkylphenol solvents

Alkylphenol solvents have been used in the production of biofuels from cellulose and corn stover [83]. In the commercial practices for the generation of levulinic acid and derivatives, levulinic acid has to be isolated from the mineral acid in order to achieve recyclability of the acid catalyst and circumvent the problems in the downstream. To obtain greater than 50% yield of levulinic acid, sulfuric acid aqueous solution is used for the degradation of cellulose. The amount of levulinic acid formed is, however, low and the recovery is costly. Furthermore, the use of a solvent such as water, which possesses a low boiling point as compared to levulinic acid, is such that, for product recovery, the solvent must be distilled. Alkylphenol solvents can be utilized to obtain selective levulinic acid mainly from sulfuric

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solution, and to obtain γ-valerolactone from water with a relatively greater partition coefficient than levulinic acid. The amount of γ-valerolactone in the alkylphenol solvent can be further enhanced by the transformation of levulinic acid into γ-valerolactone by hydrogen with the help of the carbon-supported Ru-Sn catalyst in the presence of alkylphenols without solvent hydrogenation. After obtaining levulinic acid in the presence of the alkylphenol solvent, the sulfuric acid aqueous phase can be renewed for continuous cycles for degradation of cellulose. The recovery of γ-valerolactone can be achieved from the solvent through distillation.

Ruthenium on carbon (Ru/C) could serve as an efficient catalyst. The C═C bonds in 2-s-butylphenol are hydrogenated by Ru/C, resulting in the formation of butylcyclohexanone and butylcyclohexanol. However, the Ru/C catalyst could deactivate with time in the presence of formic acid even at low temperatures. Formic acid is transformed into hydrogen and carbon dioxide, but catalyst deactivation could form ethane and carbon monoxide [82]. The hemicellulose part of a lignocellulose-based biomass can be transformed into levulinic acid and furfural in biphasic reactors having alkylphenols as a solvent, which would then selectively separate furane-based compounds from aqueous solutions of acids. A catalytic system in the presence of the alkylphenol solvent for the conversion of the cellulosic and hemicellulosic parts into fuels, with integrated subsystems for conversion of cellulose, hemicellulose, and lignin along with a subsystem designed for alkylphenol solvent recovery and the intermediates obtained from biomass, i.e., levulinic acid and γ-valerolactone, has been developed. Reduction of energy requirements is achieved via a heat exchange network (HEN), resulting in a process with a 34.8% yield for the conversion of biomass into fuels having low solid concentrations but utilizing a high amount of solvents. The HEN and the separation subsystems recover 99% of the solvents and 72% of the total heating requirements are reduced. The techno-economic analyses suggest a minimal selling price of $3.37 per gallon of gasoline, which is economical as an alternative to other methods of biofuel production [83].

5. Conclusions

Bio-based solvents are eco-friendly and biodegradable and can be produced from renewable resources. Alkylphenols are lignin-based biodegradable solvents derived mainly from lignocellulosic biomass and have great potential to be used as alternatives to other nondegradable solvents. Alkylphenols and alkyl ethoxyphenols are widely utilized in surfactant industries. However, excessive and unregulated use of alkylphenols could pose health and environmental concerns. Advances in technology and design at an industrial scale could promote application of alkylphenol solvents in a biorefinery setup for the production of biochemical and biofuels.

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